

THE DEVELOPMENT OF SAMPLING TECHNIQUES FOR
PORE WATERS IN LAKE SEDIMENTS

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May, 1998

ABSTRACT

Pore waters in lake sediments are potential recorders of past climate changes. The isotopic and chemical compositions of water in lakes are sensitive to and affected by climate parameters. Under favorable conditions, these signals can penetrate into the sediment and may be retained there for tens of thousands years.

The goal of this project is to develop sampling techniques for the analysis of isotopic composition, the chemistry and the concentrations of dissolved noble gases of pore waters. There have been three different ideas to sample for these parameters. One is *in situ* pumping of pore water using drive point profilers with a peristaltic pump. Modifications and trials were taken place to optimize the performance of the drive point sampler. It was used in summer 1997 at Sutherland Pond, BRF, NY. This method proved to be unsuccessful because the screens became clogged. The second approach uses standard coring techniques to recover lake sediments followed by subsequent separation of water and sediment by centrifugation. This technique was applied to a core from Ammersee, a lake in Germany. However, the nature of this technique does not allow the sampling of the

dissolved gases. The third method is *in situ* equilibration sampler. The small water filled chambers made of semi-permeable membranes acquire pore water samples by means of equilibration with water in the sediment. The technique was tested in laboratory in order to determine their properties in terms of diffusion of dissolved gases and ions.

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INTRODUCTION

In our efforts to understand the natural variability and habitability of the Earth, many recent researches on the climate system focus on the impacts of anthropogenic changes. The effects of these changes, however, can only be understood through a better knowledge of the past. With knowledge of the history of climate and the related changes in the entire Earth's system at a long time scale, not only can we better understand the influence of anthropogenic changes at present, but also the future of the earth's climate.

Paleoclimatology is the study of the earth's climatic changes over the past millions of years and the earth's environmental condition at that time. It is mainly a study of geological and biological records and their fluctuations over time. For the past 40 years, researches in this field have acquired significant achievements with help of new techniques and models. The major climate archives today include ice cores, deep ocean sediments, and lake sediments (Hecht, 1985). Preserved in them are fauna and flora fossils, paleo-atmospheric air, chemical elements and many more. By studying and analyzing their chemical

and physical properties, paleoclimatology sheds light into the reconstruction of the earth's environment in history.

POTENTIAL NEW ARCHIEVE

Subject of interest

The subject of interest here is pore waters in deep lake sediment. Pore waters in lake sediments are lake waters that have been trapped in sediment by sedimentation. A study by Zimmermann (1997) has shown that pore water exchange process with lake water occurs in muddy sediment over a depth of 1cm to 10cm. "Flow of water out of the sediment... was replaced by an influx of oxygenated supernatant water into the sediment close by" (Zimmermann, et al, 1997). It implies that pore water at shallow sediment resembles that in the water body. Over long period of time, under favored conditions, such pore waters are contained and buried along with sedimentation. The hypothesis proposed here is that these pore waters at deep sedimentary depth may be potential record of the lake water in the past. Since lake water is sensitive to changes in climatic parameters, studies in pore water may provide valuable paleoclimate information.

Sampling pore waters

Pore waters actually have been the interests of other scientific studies over the years. Samples of pore waters have been extracted at various locations for geochemistry and ecology studies. Major studies have been done on sampling and analyzing the ionic compositions in these pore waters. However, samples taken for these studies are all from relatively shallow depth generally less than 5 meter deep (Degarge, et al, 1994; Reeve and Perry, 1994; and others). To obtain records for paleo study, samples must be retrieved from much deeper sediment layers. Though sedimentation rates vary from site to site, in general samples should be taken over a depth of at least about 10 meter for study of approximately 10,000 years (Meanza-Gmelch, 1997) in the past.

For the purpose of this study, it is important to sample pore water at a lake that is well mixed, preferably in tropical or subtropical region where lakes do not freeze. Consequently, water at the bottom of the lake would be very similar to that at the surface so that changes in climate and their effect on lake water is more accurately recorded in pore waters. In addition can be it would be ideal if the lake has a relatively high sedimentation rate and has no inflow of water in the sediments. This will allow study of detail information in the record, and

minimize the possibility of distortion in the signals caused by groundwater and such.

Climate proxies

There are two types of indicators in lake pore waters, which are of interests. One is the isotopic composition of oxygen and hydrogen in water molecules; the other is the amount of dissolved atmospheric noble gases in pore waters.

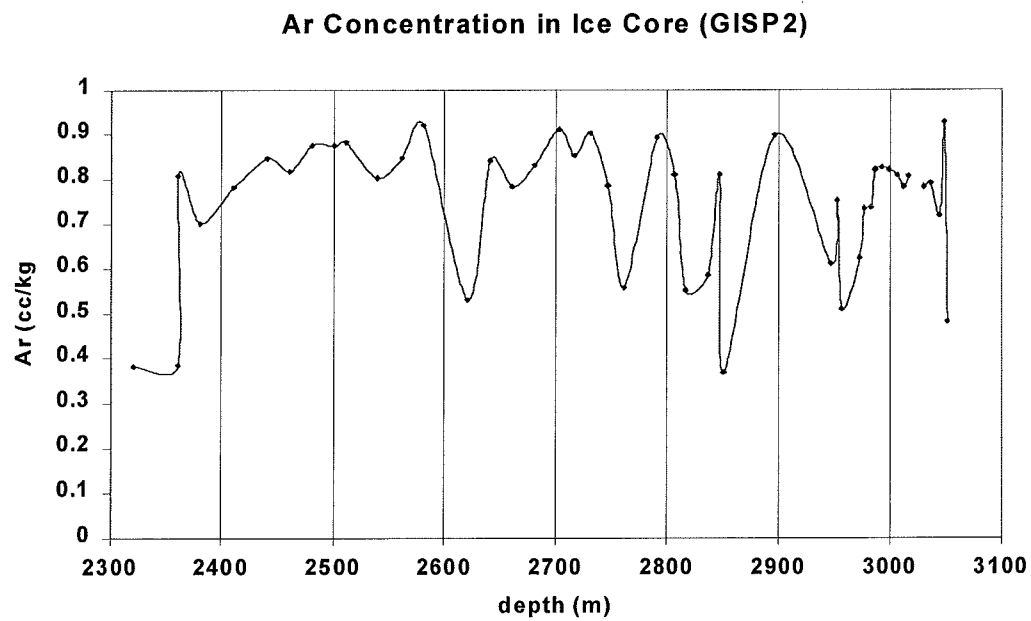
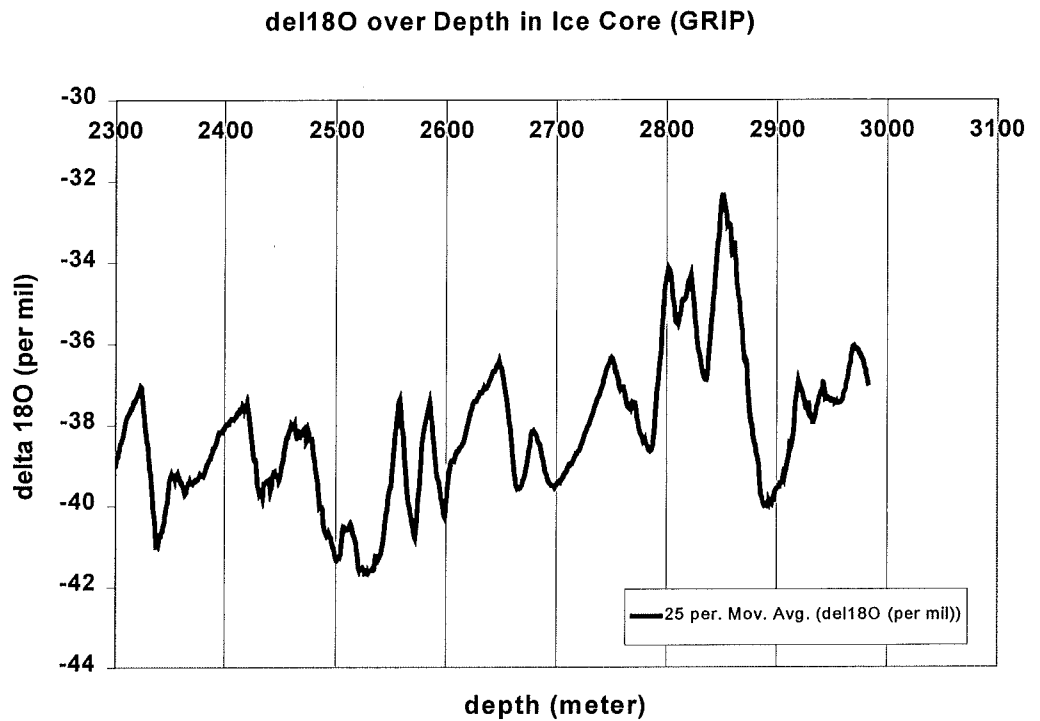
The stable isotopic composition of lake water is influenced by aridity, temperature and moisture transport regime. "The $^{18}\text{O}/^{16}\text{O}$ ratio in closed lake waters has been observed to vary as a function of the degree of evaporative concentration." (Street-Perrott and Harrison, 1985). It is measured by the per mill deviation of the concentrations of ^{18}O ($\delta^{18}\text{O}$) and ^2H (δD) in pore water from that in Standard Mean Ocean Water (SMOW). Isotopic paleoclimatology has a long well developed history. In 1947, Harold Urey suggested that the fractionation of stable isotopes was temperature dependent (Hecht, 1985). With advancing technology, stable isotope of oxygen has become a reliable climate proxy. Today, stable isotopic analyses are regularly applied in ice core water. For example, the fluctuations of $\delta^{18}\text{O}$ in water have estimated to about 10°C variation of the earth's

average atmospheric temperature in the past 150,000 years (Bigg, 31).

On the other hand, the solubility of atmospheric noble gases in water is very much temperature dependant. The concentration of noble gases in water bodies have been used in determining the local temperature in the past (Aeschbach-Hertig, et al, 1998). From ice core analysis, Argon concentration also shows a close correlation with $\delta^{18}\text{O}$ (Fig. 1). Due to increased molecular movements, solubility of gaseous molecules into water is weaker at higher temperature, and vice versa (Fig. 2). They reflect the average temperature on the lake's surface. Other dissolved atmospheric gases may react in chemical reactions, and thus changing their concentrations in pore water. But the inertness of noble gases (Ne, Ar, Kr, Xe) assures that their concentrations in pore water to be preserved, as they had been when the sedimentation was formed.

There have been three different ideas to sample this new potential archive with the climate proxies intact. These three sampling techniques are (1) *in situ* pumping; (2) conventional coring and extraction; (3) *in situ* dialysis sampling. This study is to explore the applicability of these techniques.

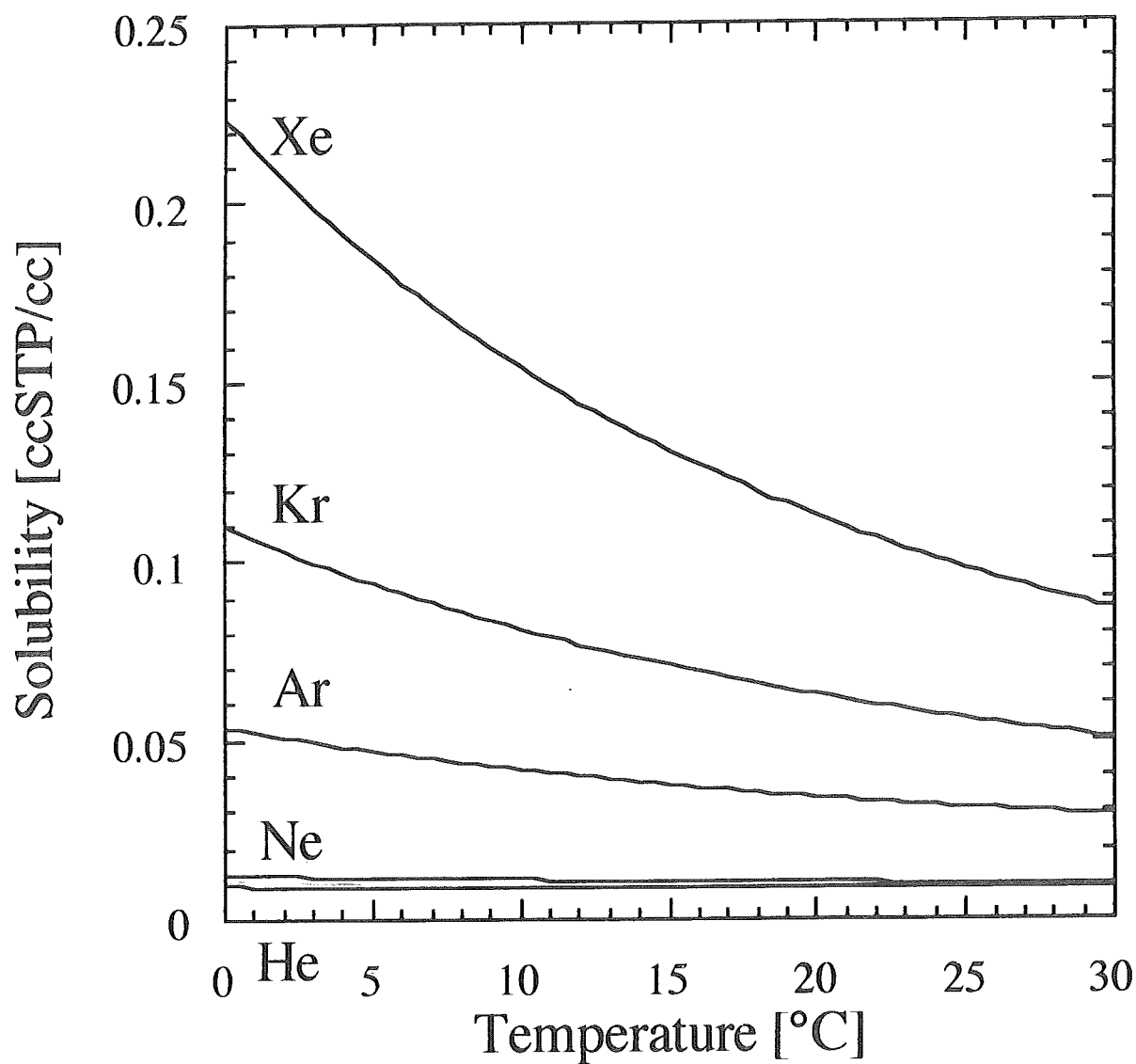
Fig. 1. Comparison of Argon Concentrations and $\delta^{18}\text{O}$ in Ice Core (GISP2).



Data obtained from the Greenland Summit Ice Cores CD-ROM
<ftp://ftp.ngdc.noaa.gov/paleo/icecore/greenland/summit/gisp2/gases/noblegas.dat>

Fig. 2. Solubility of Noble Gases in Water.

Solubilities of noble gases in water



DEVELOPMENTS OF SAMPLING TECHNIQUES

In situ pumping

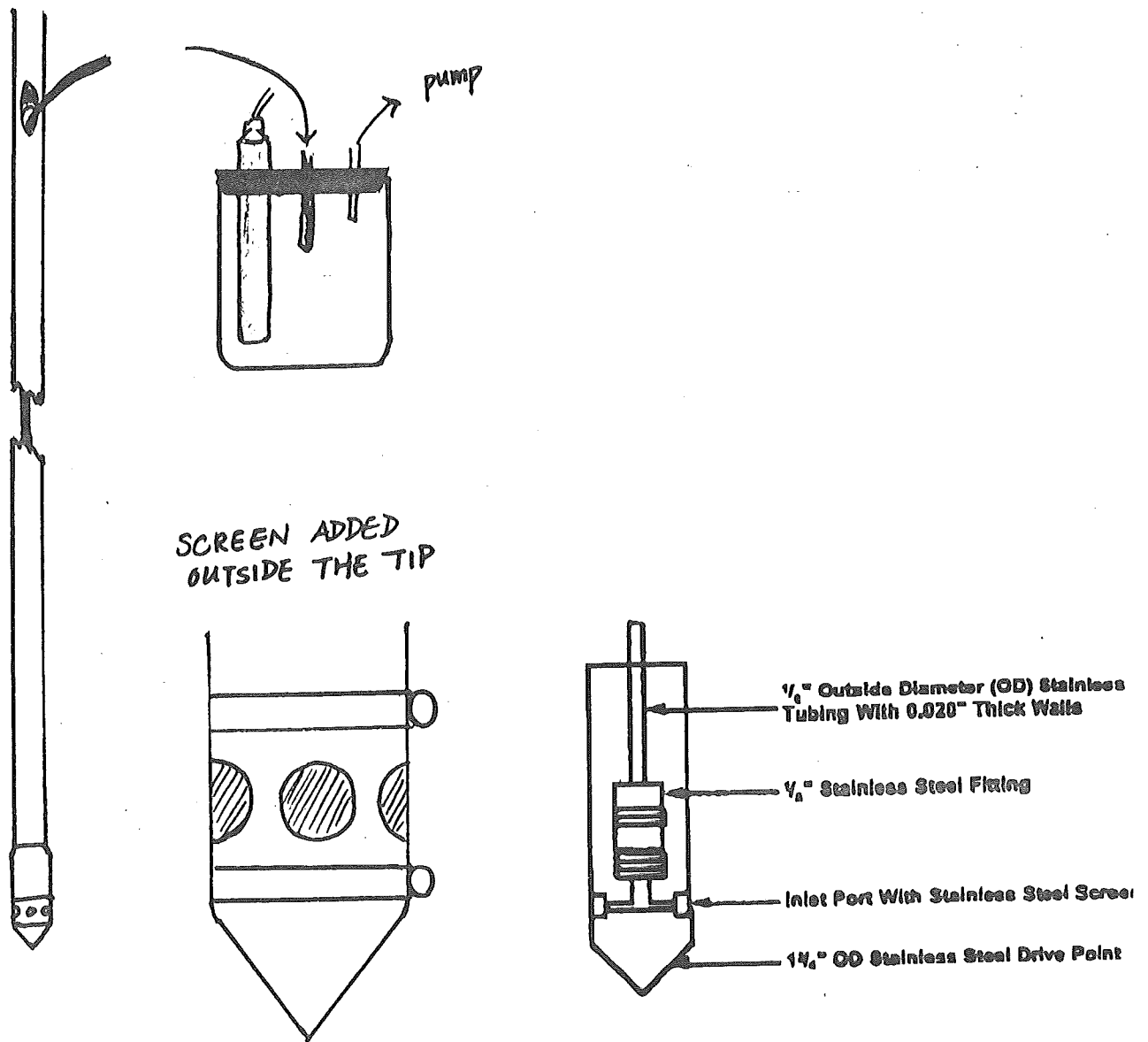
Principle

In situ pumping for pore water is a technique adapted from a groundwater sampling methodology using a drive point profiler. It has shown to be able to collect water samples in a complex hydrogeologic site including marine clay and silt (Soloyanis, et al, 1996; Broholm, et al, 1994). Water is to be pumped up directly from the surrounding through the inlet ports at the profiler's tip. It has demonstrated to obtain volatile liquid samples in complex hydrogeologic units including marine clay and silt (Soloyanis, et al, 1996). "The vertical drive point profiling method ... is a rapid, inexpensive method of obtaining groundwater samples ... and can take multiple samples in a single boring without removing equipment from the hole between samples" (Soloyanis, et al, 1996).

Methodology

The drive point profiler tip was masked with fine sized screens outside and around the inlet ports to avoid clogging (Fig. 3). The two types of screens used was first a metal screen

Fig. 3. Drive Point Profiler experiment setup.



(> 200 mesh), then a piece of fine fiber used for regular air mask. The stainless steel drive point tip was connected to a 4mm x 2.5mm LDPE tubing. The other end of the tubing was attached to a sealed sampler along with a pH meter and an outlet to handpump through another collector. The tip was connected to a series of extension rods and pressed down vertically into the sediments. It was stabilized at desired depth. Water was pumped up into the sampler. When the pH of the water became stable, the pore water was pumped over to the collector, filtered and sealed off. The pump was then reversed to push water back out *in-situ* to prevent downward transfer of water. (Broholm, et al, 1994). The profiler was then moved down to another depth. At this point, pumping and reverse pumping a small portion of pore water purged the tubing volume. It was discarded before actual samples were taken.

This method was tested numerous times in a pond at the Lamont-Dorothy Earth Observatory, NY. The drive point profiler was inserted in the sediment for a depth of less than 3 feet, and an adequate amount of water (> 5ml) was retrieved from the muddy sediment.

This sampling technique was tested in the field on August 5 ~ 6, 1997 at Sutherland Pond, a small shallow glacier lake in Black Rock Forest, NY. A floating workstation was assembled with

a drilling platform and two inflatable boats. To avoid contamination of groundwater in the samples, cold spots of possible groundwater inflows were identified by diving into the lake. The workstation was positioned at the center, deepest part of the lake, away from possible groundwater inflows. The location was stabilized with anchors dropped at each corner of the station approximately 30 ~ 50 feet away. The profiler was drawn at approximately 5, 8, 10 and 15 feet respectively, from the lake water level over the two-day field experiment. Metal screen was used for the two shallower depths at 5 and 8 feet, then the finer fiber screen was switched to for sampling of finer sediments. At the two deeper depths, both air and distilled water were pushed into the system, respectively, in attempt to unclog the screen when it became blocked (Broholm, 1994).

Results

In the first trial (5 ft.), there was a continuous stream of water pumped up. Green water plants were found attached to the clamps around the profiler tip. It indicated that the water was bottom lake water, rather than pore water. In the second trial at 8 feet below the lake level, the tip reached the sediment as indicated by the muddy residual around the tip. Only a few drops of water-sediment mixture were pumped up in the first few

minutes. No water was drawn up thereafter. The screen was found to be clogged. In the last trial at approximately 10 feet then 15 feet, no pore water could be pumped up at all, even after applying water and air trying to unblock.

Discussion

The failure of *in situ* pumping has shown that the adaptation from ground water sampling was not successful. Clogging of the screens indicates that the sediments have very fine grain sizes. They also probably have very low water contents, which added to the difficulties of sampling.

Conventional coring and extraction

Principle

The success of the second method, conventional coring followed by extraction, relies on the acquisition of the lake sediment with conventional coring technique, such as piston corer (Wright, et al, 1984). Pore water is then physically extracted from the sediment by either centrifugation or squeezing. Filtration follows to remove sedimentary suspension in the pore waters. The pore water obtained from this process can then be further analyzed for its isotopic compositions and ion contents. However, dissolved gas contents in these sediments may be changed since the sediment and pore water was exposed to air during processing.

Lake sediments at various known depth should be obtained by coring. They should be maintained in the original condition as much as possible by immediate freezing. After thawing, extraction followed by analysis should take place as soon as possible to eliminate possible contamination or evaporation.

Methodology

This method was applied to four sediment samples from Lake Ammersee in southern Germany¹. Waterdepth was 80m. Samples were taken 1 km north of the deepest part of the lake at hole number AS96-1 on October 14, 1996. The sediment samples were obtained from the bottom of each 5-meter section. They were frozen immediately after coring, and thawed on August 23, 1997.

Extraction of pore water proceeded in March 1998. A portion of each sediments was transferred from their original bottles to 50ml centrifuge tubes using spatula. The tubes were then capped tightly. Sediment samples were then centrifuged at 5,000 rpm for 2.5 hours using Silencer® (model H-103 FRS). Pore waters were poured into dried glass vials immediately after centrifugation. The glass bottles were sealed with parafilm and sent for stable isotopes. Centrifugation was repeated for a new set of sediment taken from the original bottles. The pore waters extracted were stored in plastic vials and filtered. The pore waters were diluted with 4 times distilled water to make up a 20% solution for ion analysis using the Dionex® ion chromatograph. A scheme of calibration solutions contains NaCl, NaBr, NaNO₃, HPO₃, KH₂PO₄, and NaSO₄ was used for calibrations. All solutions were manually

injected using sterile 1ml syringes. A small portion of each sediment from the second centrifugation were heated in a furnace at 375°C for 1.5 hours, weighted, then for another 1.5 hours to quantify the moisture contents in the sediments. All sediment samples were weighted before and after every step.

Results

All four sediment samples were very fine and dense in appearance. While AB was easier to be taken out by spatula, the others are harder and stickier. The weights of the sediments remained the same at the end of the second round furnaciation as at the end of the first one. The dried up sediments AB and EF were both very lightly orange in coloration. CD and CD-1 were both light gray in color.

As shown in Table 1, liquid contents in the sediments were calculated to range from 21.591% to 8.291% with increasing depths. The values of per mille deviations of both ^{18}O and deuterium (^2H) decrease with increasing depths which converts to a high fractions of the isotopes in shallower depths, and lower values in deeper sediments.

¹ Field work and sediment samples information of Lake Ammersee were provided by Dr. U.V. Grafenstein and Dr. M. Stute, and translated by Dr. M. Stute

Table 1. Pore waters from sediment samples taken from bore hole AS96-1 of Lake Ammersee, Germany²

Section/Depth (m)	Age (yr)	$\delta^{18}\text{O}^\dagger$	δD^\dagger	Liquid content (%)
AB/5	6500 BP	-10.205	-72.47	21.591
CD/10	11000 BP	-10.68	-87.35	16.778
CD-1*/12	14000 BP	-11.17	-92.67	9.843
EF/15	17000 BP	-11.615	-95.04	8.291

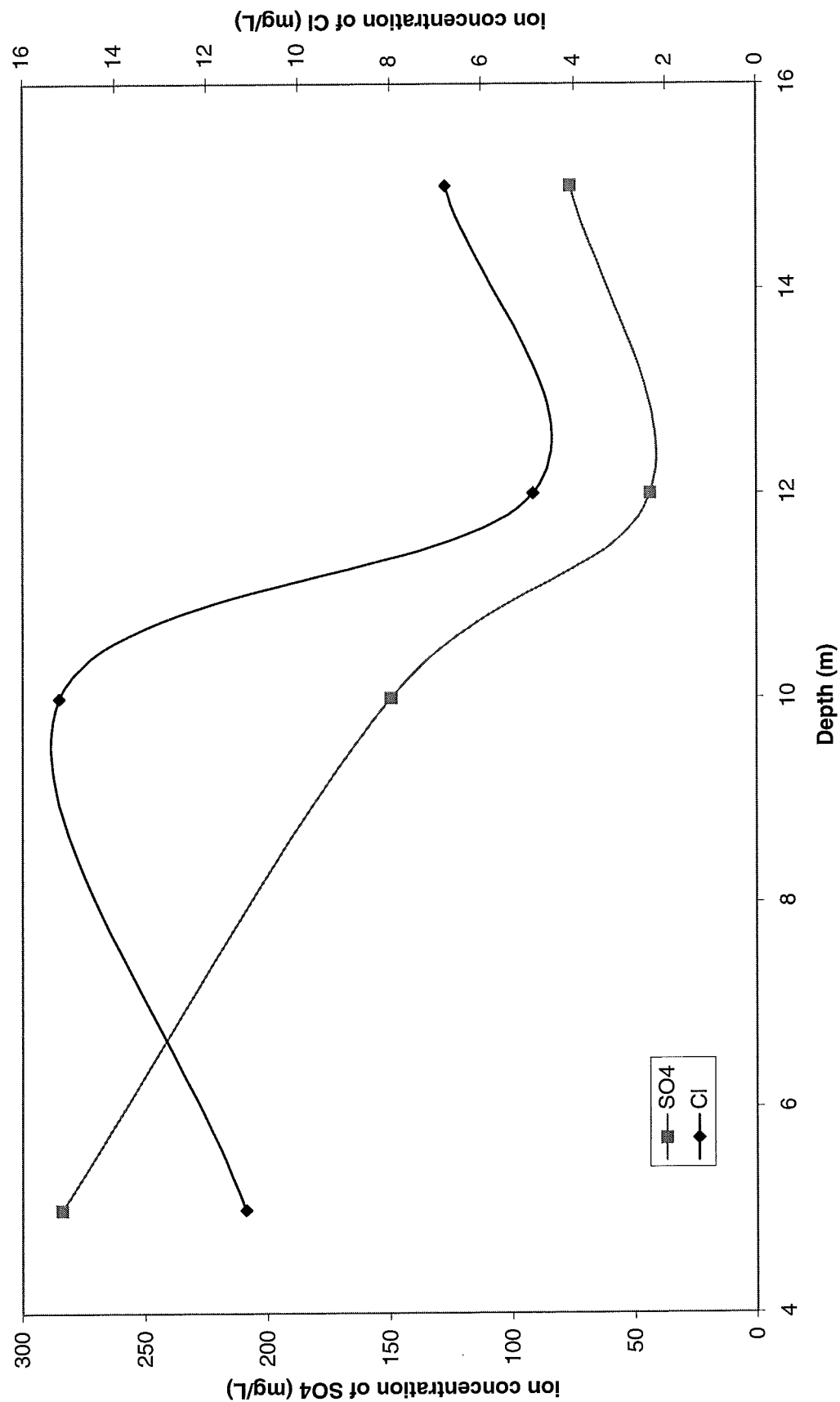
* This sediment was taken from another core AS96-1a.

† Per mille deviation of isotopes from SMOW.

The retention times of each peak in the anion chromatograph plots were compared with those in a calibration scheme. The ion contents shows there are mainly two types of anion present in the pore waters, chloride (Cl^-) and sulfate (SO_4^{2-}). Nitrate (NO_3^-) was present in section AB (16.60 mg/L) but not significant in the other sections (Table 2). The integrated areas under the peaks were converted back to their ion concentrations with calibration trendlines. The fluctuations in concentrations of Cl^- and SO_4^{2-} have similar patterns in the deeper depths (Fig. 4). Both have a lower concentration at 12m than at 15m, which then shoot up more than 3 folds at 10m depth. In the 5m pore water sample, Cl^-

² The approximated depth and age information were provided by Dr. U.V. Grafenstein and Dr. M Stute, and translated from German to English by Dr. M Stute.

Fig. 4. Chloride and Sulfate Anion Concentrations in Pore Waters (Lake Ammersee)



concentration continues to increase while SO_4^{2-} takes a dip with a lower concentration than that at 10m sample.

Table 2. Estimated Anion Concentrations of Pore Waters from Lake Ammersee, Germany

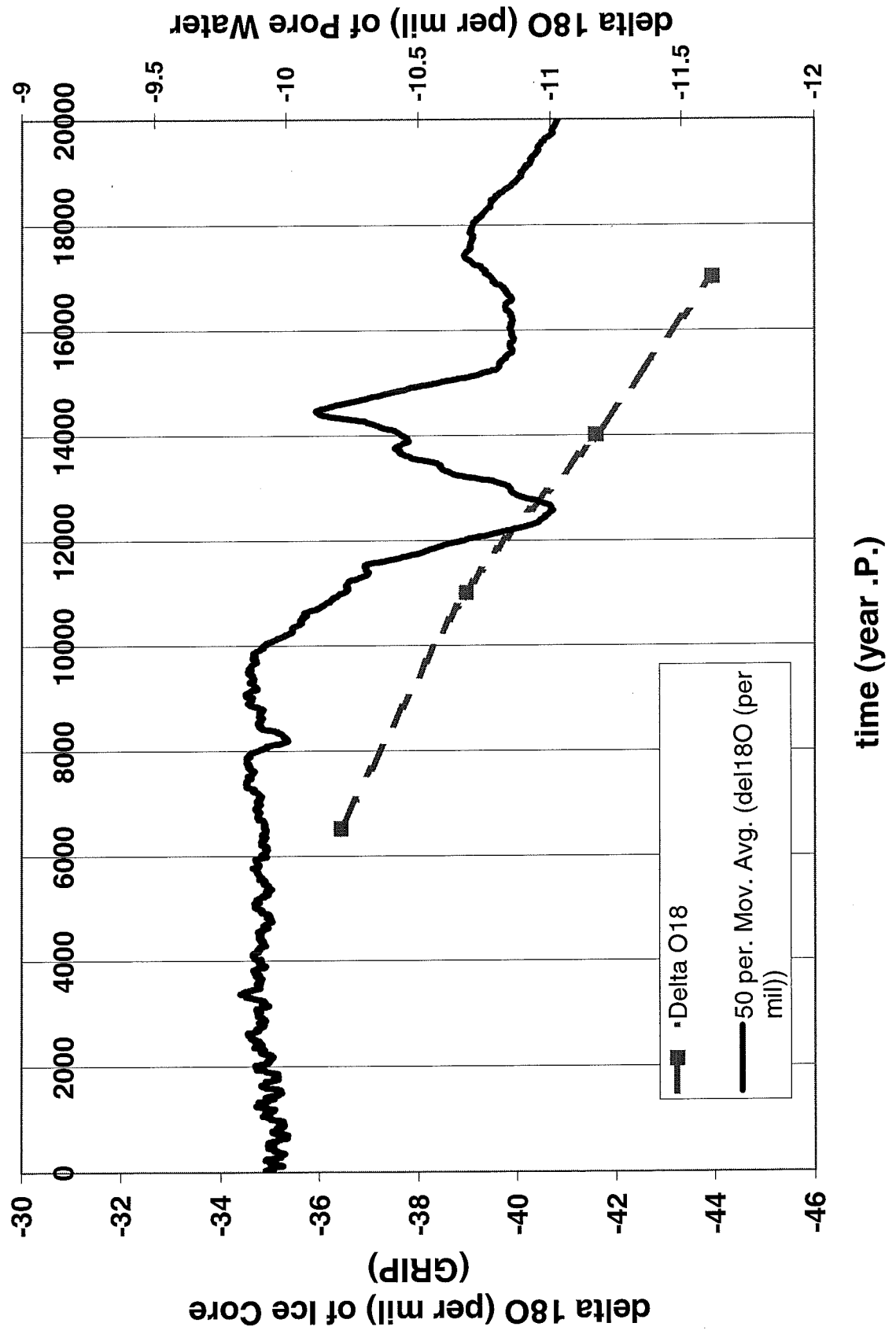
Section	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)
AB	11.14	16.60	284.05
CD	15.20	--	149.67
CD-1	4.88	--	43.62
EF	6.78	--	76.59

Discussion

The smooth physical appearances and textures of the sediments indicate that the sediments are either silt or clay with very fine grain sizes. The coloration of the sediments implies that there may be similar sedimentation at 5m and 15m. Water contents are low in 10m or deeper. Section A, on the other hand, has relatively higher percentage of liquid by weight.

The per mille deviations of ^{18}O and Deuterium from SMOW decreases over depths. This may be thought as temperature in the lake, which has been affected by aridity and climate, has been generally increasing for the period of 14,000 to 6,500 years ago. From many other records such as the $\delta^{18}\text{O}$ measurement in ice on Fig. 5, temperature in the earth's atmosphere has estimated to fluctuate quite a bit from 16,000 to 10,000 BP where the Younger

**Fig. 5. Delta18O in ice core (GRIP) and pore waters
(Lake Ammersee) over time.**



important nutrient for plants, its present indicates that there was probably an important change in the lake, which destroyed a majority of the plants leaving nitrate unused and buried with pore waters. In this section, instead of continuing with a similar pattern of changes, the directions of concentrations of chloride and sulfate diverge. Sulfate concentration continues to increase from 147.67 to 284.05 mg/L. Since sulfate is an aqueous phase reaction product of the gas sulfur dioxide, the doubling amount of sulfate observed in section AB may be an indicator of an increase in combustion, volcanic emissions and biological activity in the lake (Bigg, 102). On contrast, chloride concentration decreases from 15.20 to 11.14 mg/L. While chloride is very inactive in biological reactions and hence more conservative, it is more representative of the condition of the lake water than sulfate. The decrease in chloride concentration in section AB thus may show a higher humidity and/or low temperature at that time.

However, due to the limit data available, the results from this part of the study are not conclusive. They may only serve as hypotheses for further studies in pore water. Many more samples at smaller depth intervals are needed to construct a better picture of the changes in the climate proxies of interests.

***In situ* dialysis sampling**

Principle

In situ dialysis sampling is based on the principle of equilibration and the use of dialysis membrane. Dialysis membranes are semi-permeable allowing only small molecules diffusing across but not large molecules such as protein or sugar. Both ion and dissolved gas molecules can diffuse through such a membrane. Over time, their concentrations are equilibrated in the two environments separated by the dialysis membrane (Hesslei, 1976). "Dialysis cells in which a membrane separates distilled water from the sediment have been shown to provide good estimates of pore-water concentration" (Davison, et al, 1991). By placing a dialysis membrane sampler *in situ* over a period of time long enough for equilibrium, the sampler should contain the same kind of information in the sediment of which it has contact with.

This sampling technique is still under development, and yet to be tested in field. However, laboratory experiment has been performed to test the property of the semi-permeable dialysis membrane.

Methodology

The time required for ions to reach equilibrium was estimated in a laboratory environment during April 6 ~ 8, 1998. Cellulose Ester membrane tubing with MWCO between 12,000 ~ 14,000 Dalton was used. The wall of a small plastic bottle was substituted by a piece of the membrane, 1x7cm in surface area. 20ml of distilled water was added into the "sampler" and it was submerged into a NaCl solution (Fig. 6) The initial conductivity of the NaCl solution was 35.2mS/cm at 25.6°C.

Results

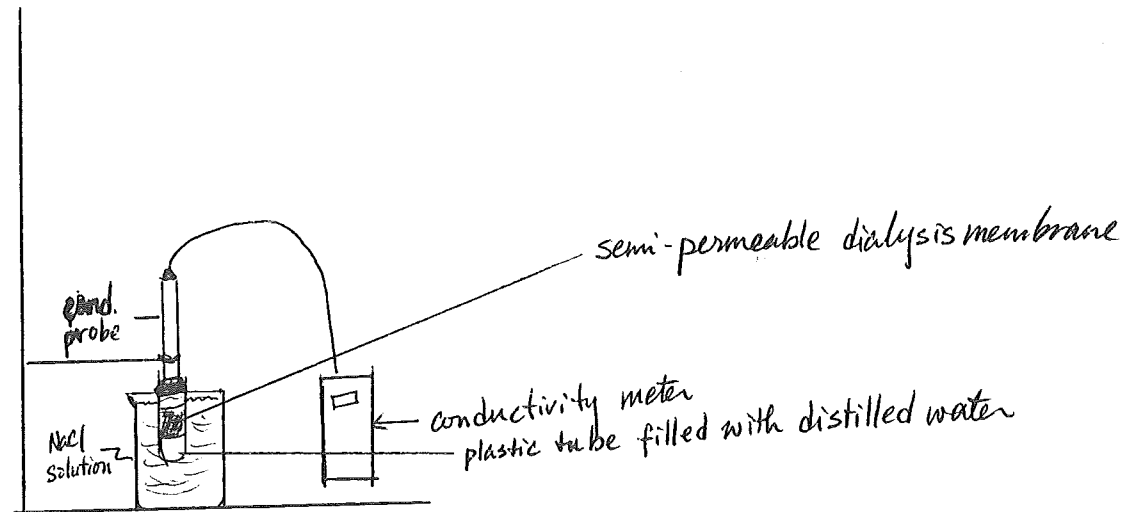
The conductivity of the water inside the sampler increased logarithmically over time (Fig. 7). By the 49th hours, conductivity inside the sampler reached 32.5mS/cm. The experiment showed that it took about 50 hours for a distilled water solution to reach equilibrium with its surrounding area with an influx area of 7cm². The surrounding NaCl solution in the beaker had a conductivity of 32.9mS/cm.

Discussion

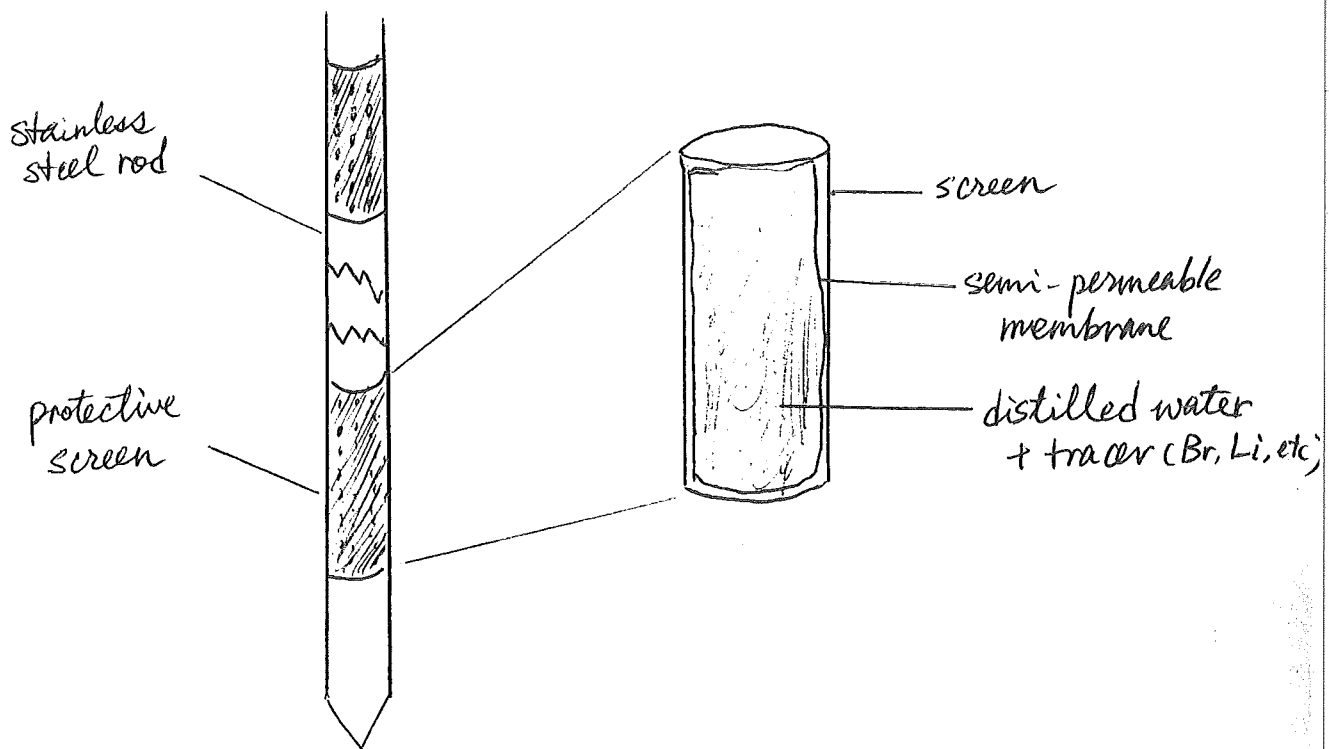
The changes in the NaCl solution are mostly due to evaporation over this long period of time in the open environment. The final conductivity of the solution in the

Fig. 6. Dialysis sampler

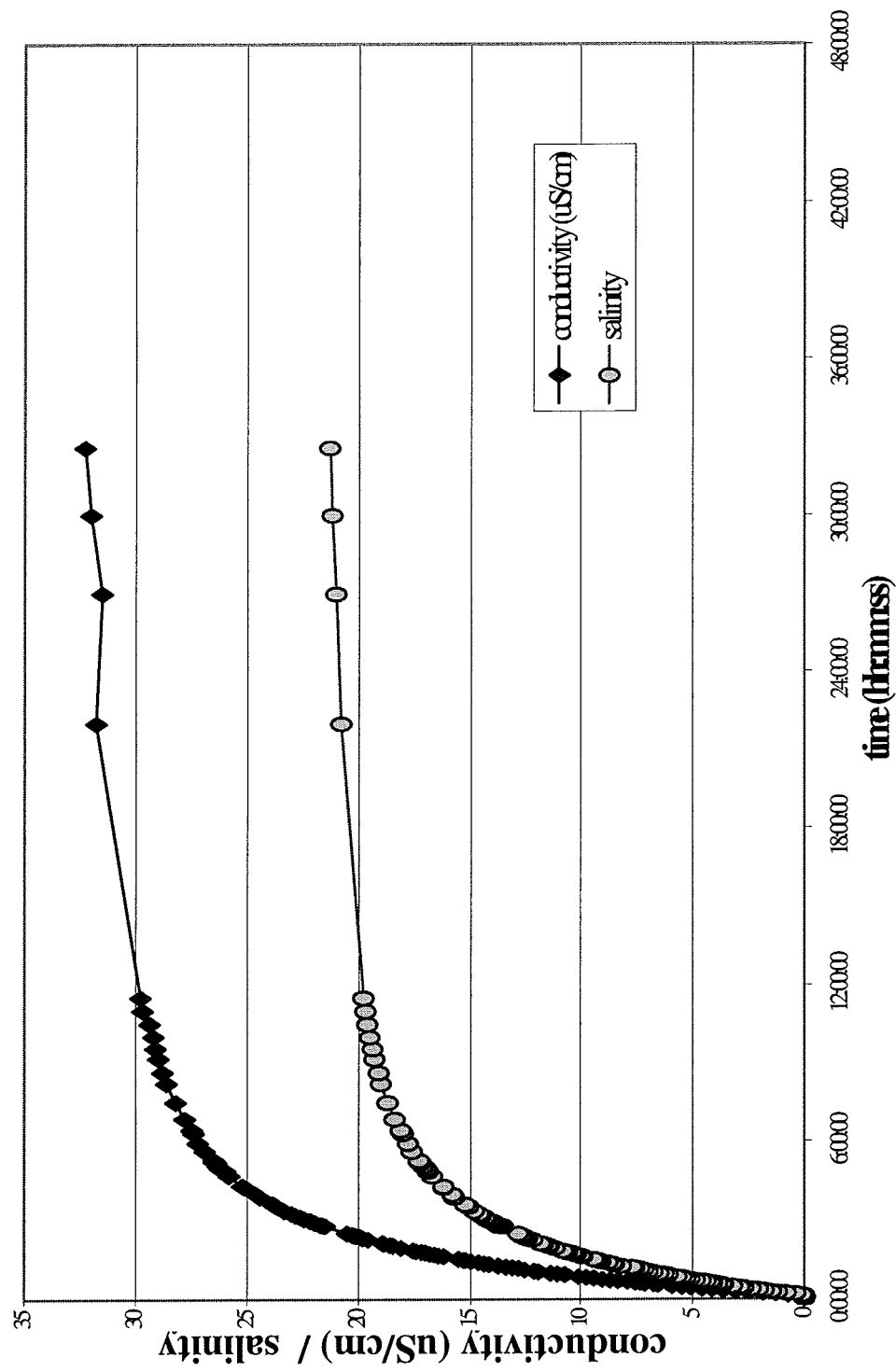
Laboratory Experiment Setup



In situ...



**Fig. 7. Conductivity and Salinity of Dialysis
Sampler in NaCl Solution**



sampler shows that equilibrium of ion concentration across the membrane required approximately 50 hours. Thus for a sampler with same parameters as the one used in the laboratory, it would take at least three days to reach a diffusion equilibrium in order to assemble a close picture of the pore water in sediment.

A sampler with a semi-permeable membrane is to be filled with distilled water with known electrical conductivity. In addition, a quantified tracer element that is not found in lake water, such as Br or Li, should be added to measure the rate of equilibrium. The sampler should be sealed completely with no air bubbles observed. Then it should be placed in sediment for a minimum of three days for equilibration. Upon retrieval, the sampler should be frozen immediately for preservation. Ion and gas analysis can be processed later after thawing the sample.

CONCLUSION

In this paper, three different approaches of pore water sampling techniques have been investigated. The methodologies and results from these techniques have shown their (potential) values to study of pore waters in deep lake sediments.

In essence, *in situ* pumping allows sampling waters at different depths within one profile. However, it has proven to be very inefficient in fine grain size sediment. Sediment with relatively low pore water content can also be difficult to operate on with this technique. Thus, unless the sediments are known as sandy with large grain sizes, *in situ* pumping is not a valuable technique for pore water sampling.

Traditional coring followed by extraction is the easiest method to obtain pore water. It is very suitable for stable isotopic and ion analysis. But due to the nature of this sampling technique, dissolved gas cannot be studied using in pore water obtained by this method.

In situ dialysis sampler is considered the alternative to direct pumping. It is, by far, the technique with the most potential values in this study. It should allow us to obtain pore water samples with dissolved gases, ions as well as stable

isotopes of various elements closely resembling those of the pore waters in lake sediment. However, this technique is much more time consuming than the others are.

RECOMMANDATION

The three sampling techniques discussed in this paper are still in their experimental phases. Improvements on the techniques and more experiments are needed to test the reliabilities of these techniques. The *in situ* dialysis sampler should be tested in field. To maximize the effort for the long period of equilibration time, each profile put *in situ* should consist of several samplers at different depths (Fig. 6). Also, traditional coring of sediments should always be taken along other techniques to have better understandings of the condition of the sediment. They can also provide more data samples for ion analysis.

ACKNOWLEDGEMENTS

I am grateful to my advisor, Dr. Martin Stute who has started the idea for this project, which interested me. He has guided me through the study, and given me valuable experience in fieldwork. He has helped me tremendously in writing of this thesis for the past year.

I warmly thank Juliet Nicoles for her technical support on ion analysis and her encouragement. This study would have been much more difficult without her help and patience. Her willingness to help has been a great support throughout the study.

I would also like to thank the Howard Hughes Research Foundation. It has financially supported me on this project for the summer of 1997.

Much gratitude is extended to my family and my friends (Hui-Yun Chen, I-ting Wu, Kathy Chow and Annie Chien). They have given me valuable advises and ideas, and even more importantly, understanding, encouragement and indispensable support during the process of thesis writing.

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GRIP Oxygen Isotopes.

<ftp://ftp.ngdc.noaa.gov/paleo/icecore/greenland/summit/gisp2/isotopes/d18o20y.dat>

GISP2 Oxygen Isotope Data.

<ftp://ftp.ngdc.noaa.gov/paleo/icecore/greenland/summit/gisp2/isotopes/gispd18o.dat>

GISP2 Ar, Kr, and Xe data.

<ftp://ftp.ngdc.noaa.gov/paleo/icecore/greenland/summit/gisp2/gases/noblegas.dat>

APPENDICES

A. Formula used

Per mille deviation of isotopes from SMOW:

$$\delta(^{18}\text{O}/^{16}\text{O})_{\text{sample}} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} - 1 \right] \times 10^3$$

B. Calibration equations for ion concentrations

Chloride (Cl^-): RT area = $2\text{E}+06$ (ion conc) - 484675

Nitrate (NO_3^-): RT = 992308 (ion conc) - 25599

Sulfate (SO_4^{2-}): RT = $1\text{E}+06$ (ion conc)

C. Operation platform

The platform is constructed mainly by two pieces of wooden board, 30"x60" each. They are put together with four beams attached at the bottom. Two aluminum rods are secured on the outer two beams for support on floatable boats. A semi circle is cut out on one of the longer side of the board for driving and boring purpose.